

Non-Equilibrium Sorption during the Movement of Pesticides in Soils

S. Baskaran,^{a*} N. S. Bolan,^a A. Rahman^b & R. W. Tillman^a

^a Department of Soil Science, Massey University, Palmerston North, New Zealand

^b AgResearch, Ruakura Agricultural Research Centre, Hamilton, New Zealand

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Abstract: Sorption and movement of two ionic herbicides (2,4-D and atrazine) and two non-ionic insecticides (phorate and terbufos) in an allophanic (Patua silt loam) and a non-allophanic (Tokomaru silt loam) soil were examined using ¹⁴C-labelled pesticides. For sorption measurements, a range of concentrations of pesticide solutions in 0.1 M calcium chloride were shaken with soil samples at a soil:solution ratio of 1:10 for 4 h at 25°C. The movement of pesticides was examined using re-packed soil columns following a step input of 2,4-D and tritiated water (³H₂O) and a pulse input of 2,4-D, atrazine, phorate and terbufos. A convection-dispersion equation (CDE), either with an equilibrium or a bicontinuum non-equilibrium sorption process, was used to simulate the measured effluent breakthrough curves (BTCs) obtained by simultaneous displacement of a non-sorbed solute (³H₂O) and a sorbed solute (2,4-D).

The Patua soil sorbed more pesticide than did the Tokomaru soil. This is attributed to the larger amounts of organic matter and the presence of short-range order clays (allophane) in the former soil compared to the latter. Kinetic sorption data for pesticides showed an initial rapid rate followed by a slower rate of sorption. In column experiments, the pesticide in the leachate appeared later in the Patua than in the Tokomaru soil. Movement of pesticides in soils decreased with an increase in *K_d* values. The step-function experiments showed a symmetrical BTC for the non-sorbed solute (³H₂O) with a sigmoidal shape, whereas there was an asymmetrical BTC with extensive tailing for the sorbed solute (2,4-D). The CDE with an equilibrium sorption process adequately described the ³H₂O BTC, but failed to simulate the BTC for 2,4-D. The CDE with a bicontinuum non-equilibrium sorption process provided a good description of the BTC for 2,4-D. Diffusion of pesticides into sorbent organic matter was considered to be the likely mechanism for the observed sorption non-equilibrium during the movement of pesticides in soils.

Key words: atrazine, 2,4-D, phorate, terbufos, isotopes, tritiated water (³H₂O), sorption, movement, transport models.

1 INTRODUCTION

There is a growing concern about the persistence of pesticide residues in soils and their subsequent movement to groundwater and surface water. Sorption of pesticides to soil particles is one of the key processes

affecting the fate of pesticides in soils.¹ The miscible displacement technique has been widely used to examine the redistribution and leaching of pesticides in soils.^{2,3} Laboratory studies using re-packed soil can help clarify the complex interactions between the physical and chemical processes involved in the movement of pesticides.²

Several mathematical models have been developed to predict the movement of pesticides in soils. These models encompass either local equilibrium sorption or

* To whom correspondence should be addressed at: Cooperative Research Centre for Soil and Land Management, PMB No. 2, Glen Osmond 5064, Australia and Department of Soil Science, University of Adelaide, Australia.

non-equilibrium sorption processes during the movement of pesticides in soil.¹ In many of the models involving local equilibrium sorption, the sorption process is often simplified by assuming that sorption attains instantaneous equilibrium and that the sorption isotherm is linear and singular.¹

It has been reported that non-equilibrium sorption is likely to occur during the movement of organic pesticides¹ and inorganic solutes⁴ in soils. The effects of non-equilibrium sorption on the movement of solutes were reviewed by Brusseau and Rao¹ and they have concluded that both physical and chemical processes cause non-equilibrium sorption of many pesticides during their movement in soils. Physical non-equilibrium is attributed mainly to the variation in the distribution of flow paths in soils,⁵⁻⁸ whereas chemical non-equilibrium involves sorbate diffusion within the matrix of sorbent organic matter (intra-organic matter diffusion) or mineral particles (intra-mineral diffusion).^{9,10}

The soils of New Zealand generally contain fairly high levels of organic carbon compared to other soils.¹¹ A number of them contain a high proportion of amorphous or short-range order clays (allophane) usually derived from volcanic material.¹² These two factors are known to have a marked influence on the sorption of pesticides in these soils.¹³ Several bioassay techniques to study the phytotoxicity, persistence and mobility of a range of herbicides have been reported in New Zealand.^{14,15} However, only a limited amount of work has been carried out on the soil-herbicide interactions in allophanic soils of New Zealand.¹³ The objectives of the present study were (i) to compare the sorption of ionic and non-ionic pesticides between an allophanic and a non-allophanic soil; (ii) to investigate the effect of sorption on the movement of pesticides in soils; and (iii) to examine the suitability of local equilibrium sorption and non-equilibrium sorption models to predict the movement of pesticides.

2 EXPERIMENTAL METHODS

2.1 Soils

Surface soil samples (0–15 cm) taken from Patua slit loam, a Typic Hapludand (medial, mesic) and Tokomaru slit loam, a Typic Fragiaqualf (fine silty, mixed, mesic) were used to examine sorption and the movement of pesticides. The Patua silt loam is an allophanic soil originating from andesitic ash, whilst the Tokomaru silt loam is a non-allophanic soil originating from siliceous loess. The soils have varying clay mineralogy, clay content,¹⁶ organic carbon,¹⁷ oxalate-extractable Fe and Al,¹⁸ and cation-exchange capacity,¹⁹ but are predominantly of low pH (Table 1).

2.2 Pesticides

The four pesticides selected for this experiment (atrazine, 2,4-D, phorate and terbufos) are used extensively in pastoral agriculture and cereal cropping in New Zealand. These pesticides include both ionic herbicides (2,4-D and atrazine) and non-ionic insecticides (phorate and terbufos). Atrazine (6-chloro-*N*²-ethyl-*N*⁴-isopropyl-1,3,5-triazine-2,4-diamine) is a weak base ($pK_a = 1.7$); 2,4-D (2,4-dichlorophenoxyacetic acid) is a weak acid ($pK_a = 2.8$); phorate (*O,O*-diethyl *S*-ethylthiomethyl phosphorodithioate) and terbufos (*S*-*tert*-butylthiomethyl *O,O*-diethyl phosphorodithioate) are non-ionic insecticides. All the pesticides used in this experiment were ¹⁴C-labelled with a radiochemical purity of >98%.

2.3 Equilibrium sorption

Sorption isotherms were determined by a standard batch equilibrium method. Sorption was measured at

TABLE 1
Soil Characteristics

Soil property	Tokomaru	Patua
USDA classification	Typic Fragiaqualf	Typic Hapludand
Parent material	Siliceous loess	Andesitic tephra
pH (1:2.5) in H ₂ O	5.80	5.56
Organic carbon (%)	3.2	8.2
Dissolved organic carbon (mg litre ⁻¹)	96	224
CEC (meq 100 g ⁻¹)	20	36
Clay (%)	24.7	18.0
Amorphous Fe oxides (%)	0.36	1.21
Amorphous Al oxides (%)	0.08	4.22
Dominant clay mineral	Mica/illite (54%) Halloysite (36%) Vermiculite (3%)	Allophane (23%) Volcanic glass (67%)

various concentrations ($\mu\text{mol litre}^{-1}$) of ^{14}C -labelled atrazine (0–74.4), 2,4-D (0–72.4), phorate (0–61.5) and terbufos (0–6.9) using 0.01 M calcium chloride as a background electrolyte. Three replicates of 1-g soil samples were equilibrated with 10 ml of pesticide solution by shaking on an end-over-end shaker for 4 h at $25 (\pm 1)^\circ\text{C}$. Preliminary experiments showed that more than 80% of the sorption occurred within 1 h. At the end of the equilibrium period, the suspension was centrifuged at $8000 \text{ rev min}^{-1}$ for 15 min and a 1-ml aliquot was taken for analysis. The ^{14}C activity of the aliquot was measured using a liquid scintillation counter. The final concentration of pesticides in the solution was calculated using the following equation:

Final concentration

$$= \frac{\text{initial concentration}}{^{14}\text{C initial}} \times ^{14}\text{C final} \quad (1)$$

This equation is valid only if it is assumed that the pesticide has not been degraded and all the ^{14}C remains associated with the parent compound. Measurement of ^{14}C -labelled pesticides remaining in the soil after sorption and subsequent mass-balance calculation indicated that there was no evidence for degradation of pesticides within the 4-h equilibration period. The amount of pesticide sorbed was calculated as the difference between the initial and the final concentration of pesticide in solution.

2.4 Kinetics of pesticide sorption

Kinetics of pesticide sorption were measured using the Patua soil for only two pesticides, one representing the ionic (2,4-D) and one the non-ionic (phorate) groups. Soil samples were shaken with calcium chloride solution (0.01 M) containing a known concentration (4 mg litre^{-1}) of pesticides on an end-over-end shaker at a soil:solution ratio of 1:10 for various periods ranging from 5 min to 960 min. The amounts of ^{14}C pesticide remaining in the solution and retained by the soil were measured after the sorption measurements. The mass balance calculations indicated recoveries of 99 to 101% and there was no evidence for loss of 2,4-D or phorate within the periods used for the kinetic study.

2.5 Column experiments

Two types of column experiment were conducted to examine the movement of pesticides in soils. One involved a step-function experiment in which a known volume of pesticide solution at a constant concentration was introduced into the soil. The applied pesticide solution was subsequently displaced through the soil column with pesticide-free solution. The other involved

a pulse experiment in which a pulse of pesticide added to the soil column was leached with a known amount of pesticide-free solution and the concentration of pesticide in both the leachate and the soil column was measured. Both the step function and the pulse experiments were carried out using re-packed soil columns.

2.5.1 Step function experiment

For this experiment, PVC tubes ($200 \text{ mm} \times 51.2 \text{ mm ID}$) were used to examine the movement of ^{14}C 2,4-D in the Patua and the Tokomaru soils. The base of the columns were sealed with a nylon mesh with an effective pore diameter of $60 \mu\text{m}$ to retain the soil in the column. The columns were packed to bulk densities of 0.88 and 1.05 Mg m^{-3} for the Patua and the Tokomaru soils, respectively, with 140 mm soil depth. The columns were covered with a plastic cap to prevent evaporation. Each cap had three pinholes through which the hypodermic needles were inserted to drip the solution at the centre of the column. Acid-washed sand was used to cover the soil surface, so that the flow from the hypodermic needles would be spread evenly over the core area.

Initially the columns were saturated with two pore volumes of 0.01 M calcium chloride. Then a known concentration of ^{14}C 2,4-D (5 mg litre^{-1}) along with tritiated water ($^3\text{H}_2\text{O}$) (67 kBq ml^{-1}) was added to the soil columns as a step-change input at a constant flux (0.25 ml min^{-1}) using a peristaltic pump. The $^3\text{H}_2\text{O}$ was used as a conservative tracer to study the movement of non-sorbed solute in the soil column. After passing seven and 35 pore volumes of input solution through the Tokomaru and the Patua soils, respectively, the applied 2,4-D and $^3\text{H}_2\text{O}$ were displaced through the soil column with similar pore volumes of 0.01 M calcium chloride to initiate desorption. The leachates from the soil columns were collected using an automatic fraction collector. The activities of $^3\text{H}_2\text{O}$ and ^{14}C in the leachate were measured using a liquid scintillation counter for dual labelling.²⁰ The maximum separations of $^3\text{H}_2\text{O}$ and ^{14}C were achieved in channel 1 (0–400) and channel 2 (400–670), respectively. In order to account for interference of one isotope with the other, simultaneous equations were derived and solved to ascertain the true counts of each isotope. At the end of the experiment the soil samples were analysed for ^{14}C 2,4-D.²¹ The soil samples were extracted using a scintillation cocktail and the cocktail containing the organic solvent (toluene) was directly assayed using the liquid scintillation counter.

2.5.2 Pulse experiment

Using the pulse experiment, the movement of ^{14}C -labelled atrazine, 2,4-D, phorate and terbufos was examined in the Patua and the Tokomaru soils. Borosilicate glass columns ($200 \text{ mm} \times 27.2 \text{ mm ID}$) were used in these experiments. A preliminary study had shown that phorate and terbufos sorbed on to walls

made of polyethylene materials, whereas negligible amounts sorbed on to glass materials. The columns were packed to a similar bulk density as for the step-input experiment. The columns were preleached with two pore volumes of 0.01 M calcium chloride, then a 5-ml pulse of ^{14}C -labelled pesticide (4 mg litre $^{-1}$ of atrazine, 2,4-D, phorate or 2 mg litre $^{-1}$ of terbufos) was applied at the top of each soil column. The columns were immediately leached with 0.01 M calcium chloride at a constant flux (0.2 ml min $^{-1}$) using a peristaltic pump. After completion of leaching, the soil columns were sectioned into 2-cm sections. The activities of ^{14}C in leachate and in the soil were measured as before and the mass balance was calculated.

2.6 Simulation of breakthrough curves

The convection-dispersion equation (CDE), coupled with descriptions of either equilibrium sorption or non-equilibrium sorption processes, was used to simulate the movement of pesticides in soils. A brief description of these models follows.

2.6.1 Equilibrium sorption model

The convection-dispersion equation (CDE) has often been used to describe one-dimensional movement of a solute in a packed soil column:²²

$$\partial C/\partial t = D \partial^2 C/\partial x^2 - v \partial C/\partial x \quad (2)$$

where C is solution concentration of the solute ($\mu\text{mol litre}^{-1}$), v is average pore water velocity (mm h^{-1}), t is time (h), D is dispersion/diffusion coefficient ($\text{mm}^2 \text{h}^{-1}$), x is the distance (mm). Various physical, chemical and biological processes have been shown to affect the movement of pesticides in soils, of which sorption is one of the most important. Additional terms are included in CDE to account for solute sorption. For an equilibrium sorption condition, the transport of a sorbed solute by convection and dispersion is described by

$$R \partial C/\partial t = D \partial^2 C/\partial x^2 - v \partial C/\partial x \quad (3)$$

where R is the retardation factor which is used as an index of the mobility of the solute.

The sorption of solutes can be represented by the following linear (eqn (4)) and non-linear Freundlich (eqn. (5)) equations:

$$S = K_d C \quad (4)$$

$$S = KC^N \quad (5)$$

Where S is the sorbed concentration of the solute ($\mu\text{mole kg}^{-1}$), K_d is the distribution coefficient and K and N are Freundlich constants. For linear sorption (eqn (4)), R becomes:

$$R = 1 + (\rho/\theta)K_d \quad (6)$$

where ρ is bulk density of soil (Mg m^{-3}) and θ is volumetric water content ($\text{mm}^3 \text{mm}^{-3}$).

For non-linear sorption (eqn (5)), R is concentration-dependent and is given by:

$$R = 1 + (\rho/\theta)KNC^{N-1} \quad (7)$$

2.6.2 Non-equilibrium bicontinuum sorption model

Bicontinuum sorption models, often referred to as 'two-site' models, have been used to represent chemical non-equilibrium. This model is conceptually similar to the 'two-region' model in which the soil water is partitioned into mobile and immobile phases.⁸ In this study, a bicontinuum sorption model was used to fit the experimental BTC for 2,4-D. According to this model, the sorbent is assumed to consist of two different types of sorption site and the sorption is instantaneous for a fraction of the sorbent (eqn (8)) and rate-limited for the remainder (eqn (9)).

$$S_1 = FKC \quad (8)$$

$$\partial S_2/\partial t = k_1 S_1 - k_2 S_2 \quad (9)$$

where S_1 and S_2 are the sorbed concentrations on type 1 and type 2 sites, respectively, F is the fraction of type 1 sites and k_1 and k_2 are the forward and the reverse first-order rate coefficients for sorption on type 2 sites.²³

Substitution of these two equations in eqn (3) and subsequent rearrangement gives

$$\begin{aligned} \partial C^*/\partial p + (\beta R - 1)NC^{*(N-1)} \partial C^*/\partial p + (1 - \beta)R \partial S^*/\partial p \\ = (1/P)(\partial^2 C^*/\partial X^2) - \partial C^*/\partial X \end{aligned} \quad (10)$$

$$(1 - \beta)R \partial S^*/\partial p = \omega(C^{*N} - S^*) \quad (11)$$

Where P is the Peclet number, L is column length (mm), p is pore volume, β is the fraction of instantaneous retardation, ω is the Damkohler number, which is a ratio of hydrodynamic residence time to characteristic time for sorption. The nondimensional parameters in eqns (10) and (11) are defined as follows.

$$C^* = C/C_0 \quad (12a)$$

$$P = vL/D \quad (12b)$$

$$S^* = [S_2/(1 - F)KNC_0^{N-1}] \quad (12c)$$

$$R = [1 + (\rho/\theta)KNC_0^{N-1}] \quad (12d)$$

$$p = vt/L \quad (12e)$$

$$\beta = [1 + F(\rho/\theta)KNC_0^{N-1}] \quad (12f)$$

$$\omega = k_2(1 - \beta)RL/v \quad (12g)$$

2.7 Model parameter estimation

A number of parameters need to be estimated to run the bicontinuum non-equilibrium model. These parameters include: Peclet number (P), retardation factor (R), frac-

tion of instantaneous retardation (β) and Damkohler number (ω). Model parameters were determined using a nonlinear least-squares optimization program.²⁴

The P value incorporates any dispersion resulting from non-equilibrium sorption as well as that from hydrodynamic dispersion.¹ The P value describes the shape of the BTC (i.e. magnitude of dispersion) and the R value describes its position (relative to the mean velocity of water).¹ The P value was determined by fitting the nonlinear least-squares optimization program to the BTC of a non-sorbed solute ($^3\text{H}_2\text{O}$), with R set to unity. The value of R for the pesticide was calculated (eqn (12d)) by using the measured sorption isotherm parameters, K and N (Table 2) and bulk density (ρ) and volumetric soil-water content (θ) values from the soil column experiments. With the values of P and R fixed, the non-equilibrium sorption parameters (ω and β) for the sorbed solute (2,4-D) were optimized to obtain the best fit to the experimental BTC. The solute transport equations (10) and (11) were solved under constant solute flux boundary conditions by finite-difference method. The model parameter values are presented in Table 3.

3 RESULTS AND DISCUSSION

3.1 Sorption isotherm

The sorption isotherms of the pesticides for the two soils are presented in Fig. 1. Sorption of pesticides was

greater in the Patua than in the Tokomaru soil. The Patua soil contained a large amount of organic carbon and a significant amount of short-range order clays (allophane) whereas the Tokomaru soil contained less organic carbon and was dominated by mica/illite (Table 1). It has been observed that soils containing large amounts of organic carbon and short-range order clays such as allophane sorb more pesticide than soils containing smaller amounts of organic carbon and crystalline clays.^{25,26}

The sorption of pesticides is adequately described by the Freundlich equation (eqn (5)) with an R^2 value >0.97 . The parameters of the Freundlich sorption isotherms for the soils are given in Table 2. The N values ranged from 0.79 to 0.98. In pesticide transport studies, the value of N has, for convenience, frequently been assumed to be equal to one (linear isotherm). Assuming $N = 1$, the distribution coefficient (K_d) was calculated (Table 2). The K_d values indicate that, in general, sorption of non-ionic pesticides was greater than that of ionic pesticides.

3.2 Kinetics of pesticide sorption

Sorption versus time plots for 2,4-D and phorate in the Patua soil are presented in Fig. 2. From this figure, it is evident that 90% of sorption of pesticides had occurred within 4 h, the period used for equilibrium sorption. Sorption in this soil was rapid and more than 75% of maximum sorption occurred within the first hour.

TABLE 2
Parameters of Freundlich Equation and the Distribution Coefficient (K_d) of the Pesticides

Pesticide	Freundlich parameter				Distribution coefficient (K_d)	
	K		N			
	Tokomaru	Patua	Tokomaru	Patua	Tokomaru	Patua
2,4-D	3.43	17.42	0.79	0.84	1.52	9.60
Atrazine	2.69	2.96	0.98	0.92	2.50	2.00
Phorate	20.01	33.63	0.94	0.90	17.42	30.28
Terbufos	24.42	35.03	0.87	0.97	18.50	33.45

TABLE 3
Mass Balance of Pesticides in the Soil Column—Pulse Experiment

Pesticide	^{14}C recovery (%)			
	Tokomaru		Patua	
	Leachate	Soil column	Leachate	Soil column
2,4-D	43 (± 2)	55 (± 10)	12 (± 3)	82 (± 8)
Atrazine	28 (± 4)	65 (± 8)	22 (± 5)	69 (± 6)
Phorate	6 (± 1)	90 (± 12)	ND ^a	93 (± 2)
Terbufos	5 (± 2)	87 (± 7)	ND ^a	96 (± 4)

^a Not detectable.

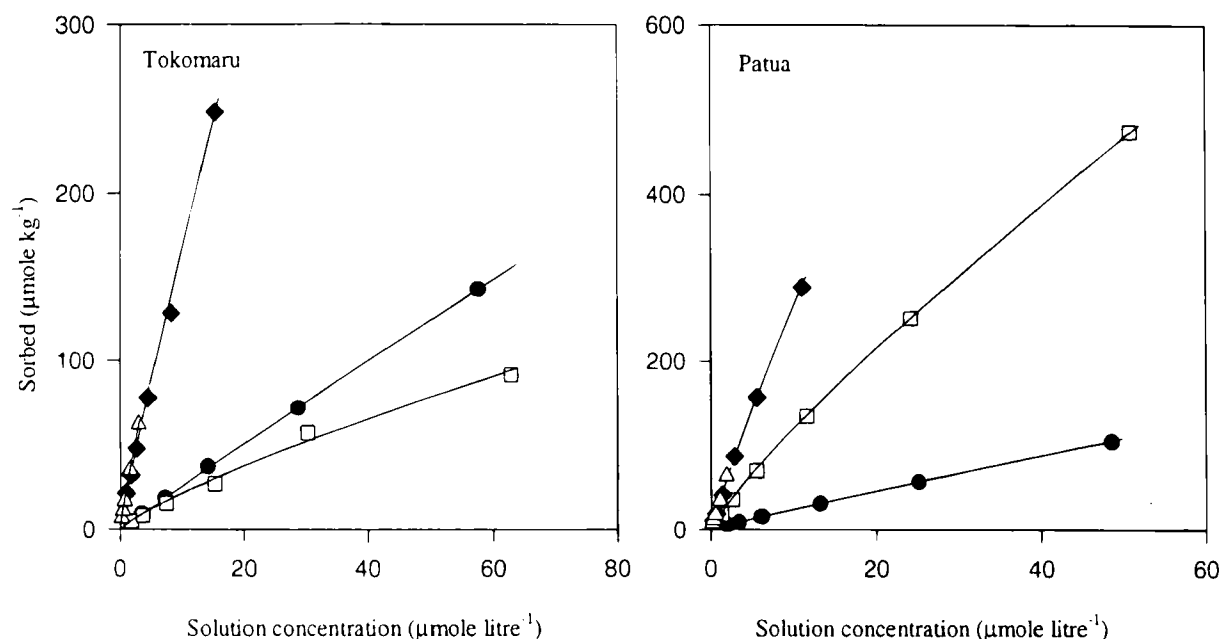


Fig. 1. Equilibrium pesticide sorption by the Tokomaru and the Patua soils: (●) atrazine, (□) 2,4-D, (◆) phorate, (△) terbufos.

However, sorption proceeded at a slower rate after 4 h. The results show sorption to be a two-stage process with a short initial phase of rapid sorption, followed by an extended period of slower sorption. Similar sorption behaviour has also been observed for other organic pesticides^{27,28} and for inorganic solutes such as cadmium⁴ using batch experiments.

Sorption of pesticide was plotted as a function of the square root of time (Fig. 2 insert). Sorption beyond 2 h

of shaking followed a square root of time relation. This suggests that at least two types of sorption site are present in this soil. Leenheer and Ahlrichs²⁹ studied sorption-rate curves of carbaryl and parathion insecticides on organic matter and found a square root time relation for periods greater than 10 min. In their experiments, the initial rapid rate of sorption appeared to be on the external surface of the sorbents and, as sorption proceeded, rates slowed and sorption was by diffusion

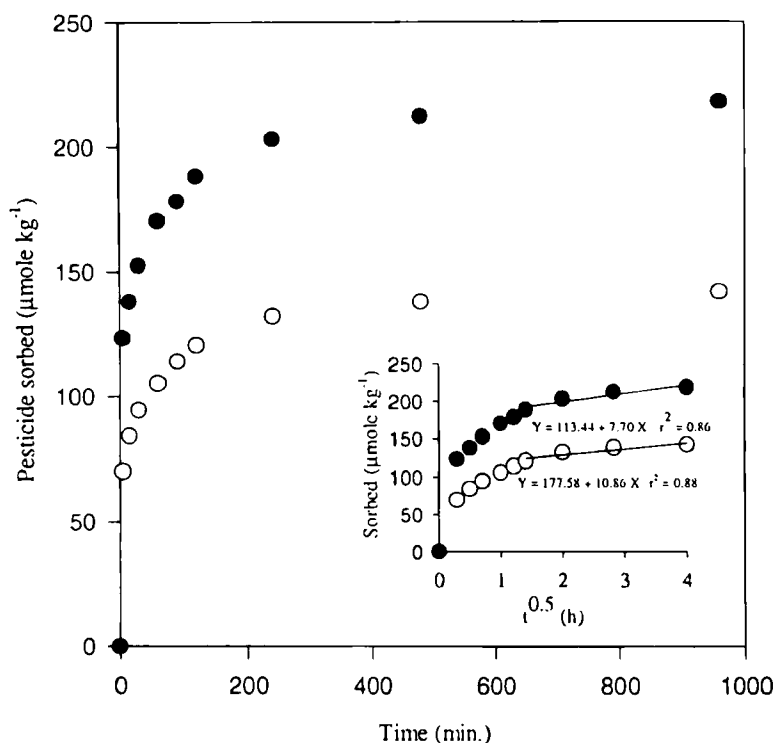


Fig. 2. Sorption kinetic data of (○) 2,4-D and (●) phorate in the Patua soil. Insert shows the rate curve as a function of square root of time. The symbols represent the measured data and the lines represent the fitted line.

onto internal sites. A similar phenomenon was observed by Khan³⁰ for the sorption of 2,4-D and picloram on humic acid in a batch experiment. In this case, the square root of time relation was linear after about 1.5 h. It was reported that the initial rapid sorption was on the surface of humic acid and the rate-limiting process was interpreted to be intra-particle diffusion into the interior of the humic acid. Recently Kookana *et al.*⁴ also observed a square root of time relation for cadmium sorption after 10 h of shaking, using a batch method.

3.3 Column experiments

3.3.1 Pulse experiment

The results of the pulse experiment are shown in Table 3. In this experiment effectively all the applied ¹⁴C-pesticides were recovered in either the leachate or the extractions from the segmented soil column (90–98%). In the Tokomaru soil, 28% of atrazine and 43% of 2,4-D were found in the leachate, whereas only small amounts of phorate and terbufos (<6%) were leached through the soil. However, in Patua soil, small amounts of atrazine (22%) and 2,4-D (12%) were found in the leachate, whereas phorate and terbufos were not detected in the leachate. Measurement of the residual pesticides in the soil indicated that most of the added phorate and terbufos remained in the soil column. In general the non-ionic pesticides (phorate and terbufos) were relatively less mobile than the ionic pesticides (atrazine and 2,4-D). Non-ionic pesticides are hydro-

phobic ($\log K_{ow} > 3.3$) with a low water solubility, and consequently sorption affinity for soil organic matter is high and these compounds are less mobile than the ionic pesticides.

Most of the pesticide residues remaining in the soil column were retained in the top-2cm layer and larger amounts of non-ionic (phorate and terbufos) than ionic (atrazine and 2,4-D) pesticides were retained in this section. These results suggest that the mobility of atrazine and 2,4-D was greater than that of phorate and terbufos. As expected from the K_d values, the retention of pesticides in the upper layer (2 cm) was greater in the Patua than in the Tokomaru soil. An inverse relationship between the K_d values of the pesticides calculated from the batch experiment and the percentage of ¹⁴C-pesticides recovered from the leachate in the pulse experiment (Fig. 3) suggested that sorption was the key process controlling the movement of pesticide. Recently Riise *et al.*³¹ reported an inverse relationship between batch sorption coefficient and the percentage of atrazine and tribenuron-methyl leached.

3.3.2 Step-function experiment

Breakthrough curves for the step-function experiments are presented in Fig. 4. A shift of the BTC of the test solute (2,4-D) to the right of that for a non-sorbed solute (³H₂O) indicates increased sorption, and thus a decreased mobility. As would be expected from the batch-sorption data, 2,4-D appeared later in the leachate from the Patua silt loam column than from the Tokomaru silt loam column. A greater shift of the BTC

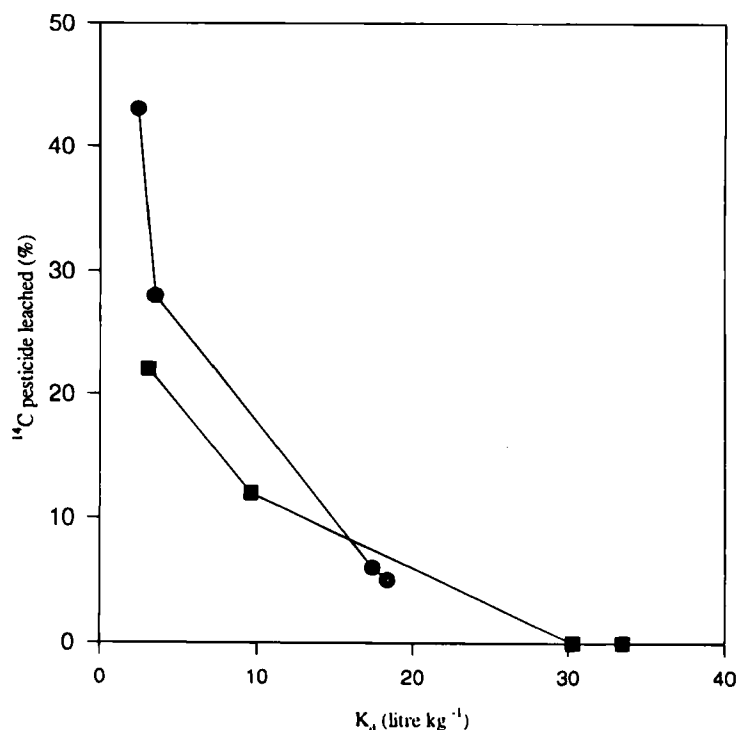


Fig. 3. Relationship between distribution coefficient (K_d) and the percentage of pesticide leached in (●) Tokomaru and (■) Patua soils.

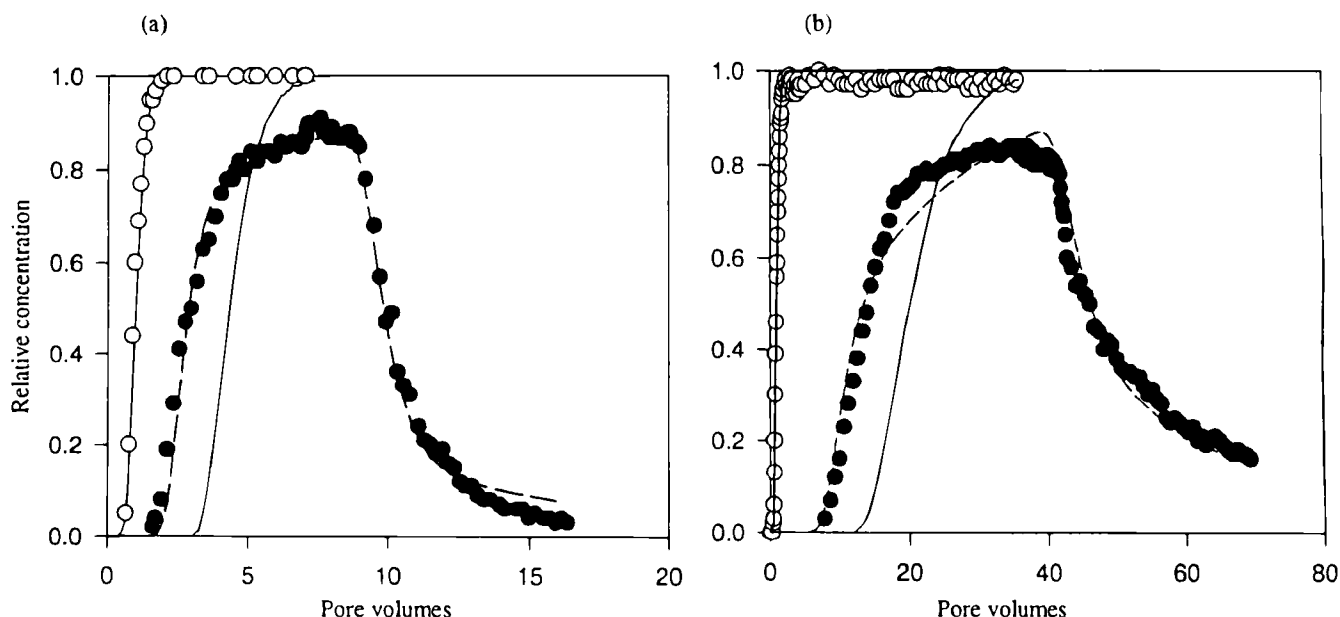


Fig. 4. BTC for (○) $^3\text{H}_2\text{O}$ and (●) 2,4-D in (a) Tokomaru and (b) Patua soils. The symbols represent the measured data and the lines represent the simulated data; (—) equilibrium sorption, (---) non-equilibrium sorption.

of 2,4-D to the right indicates increased sorption, thus a decreased mobility in the Patua soil.

It has been reported that the position of the BTC for a sorbed solute is governed by the extent of sorption, whereas the shape of the BTC is defined by the kinetics of the sorption-desorption process.¹ The BTCs for the non-sorbed solute ($^3\text{H}_2\text{O}$) were symmetrical and sigmoidal in shape, which suggests the absence of physical non-equilibrium processes in the porous medium.^{1,32} The experimental BTC for 2,4-D is asymmetrical in shape, with extensive tailing when C/C_0 approached 1.0 and again when C/C_0 approached 0.

Tailing is a common feature of BTCs, and has been attributed to a wide range of physical and chemical processes.³² In the absence of physical non-equilibrium, as evident from the $^3\text{H}_2\text{O}$ BTC, the possible reasons for the observed tailing of the BTC for the sorbed solute (2,4-D) include: (i) non-equilibrium sorption during flow due to kinetic sorption reactions;⁷ (ii) a non-singular sorption-desorption isotherm (i.e. hysteresis effect);^{33,34} and (iii) a non-linear sorption isotherm. Since the sorption-desorption isotherm for 2,4-D is near linear and near singular, the tailing of the BTC for 2,4-D is assumed to be mainly due to non-equilibrium sorption. It has been shown that a non-singular isotherm has less effect than non-equilibrium sorption on tailing of the BTC.⁶

3.4 Simulation of breakthrough curves

The CDE model with either an equilibrium sorption process (eqn (3)) or bicontinuum non-equilibrium sorption was tested for the BTCs of $^3\text{H}_2\text{O}$ and 2,4-D in the Tokomaru and the Patua soils. Comparison of the experimental and simulated BTCs using these two sorp-

tion models is shown in Fig. 4. In the case of the equilibrium sorption model a close agreement between the simulated and the experimental BTC was observed for the non-sorbed solute ($^3\text{H}_2\text{O}$), whereas considerable deviation was observed for the sorbed solute (2,4-D) (Figs 4(a) & (b)). The experimental BTC showed that the sorbed solute (2,4-D) appeared much earlier in the effluent than predicted by the model. In the present study, a symmetrical BTC was observed for $^3\text{H}_2\text{O}$, whereas an asymmetrical BTC was observed for 2,4-D. According to Rao and Davidson,³ for sorbed solutes with linear and singular sorption isotherms, symmetrical BTCs are obtained where sorption is an instantaneous equilibrium condition and asymmetrical BTCs are obtained where sorption is in non-equilibrium condition. It has been reported that a simple CDE model with an equilibrium sorption process is capable of predicting a symmetrical BTC, whereas it fails to predict an asymmetrical BTC.²

The failure of the CDE model with an equilibrium sorption process to describe the experimental BTCs for 2,4-D clearly showed that the non-equilibrium is affecting the movement of pesticides in the present experiment. Comparison of the experimental and the simulated BTCs for 2,4-D (Figs 4(a) & (b)) using the bicontinuum non-equilibrium sorption model reveals that this model provided a good description of the data. The simulations were made using the nonlinear sorption isotherm, with N values of 0.79 in the Tokomaru and 0.84 in the Patua soil. To investigate the impact of nonlinearity, simulations of the BTC for 2,4-D obtained for the two soils using the nonlinear ($N = 0.79$ and 0.84) and linear ($N = 1$) isotherms were compared (Fig. 5). It is apparent that there is little difference whether N was taken as either 0.79/0.84 or 1. This relative insignifi-

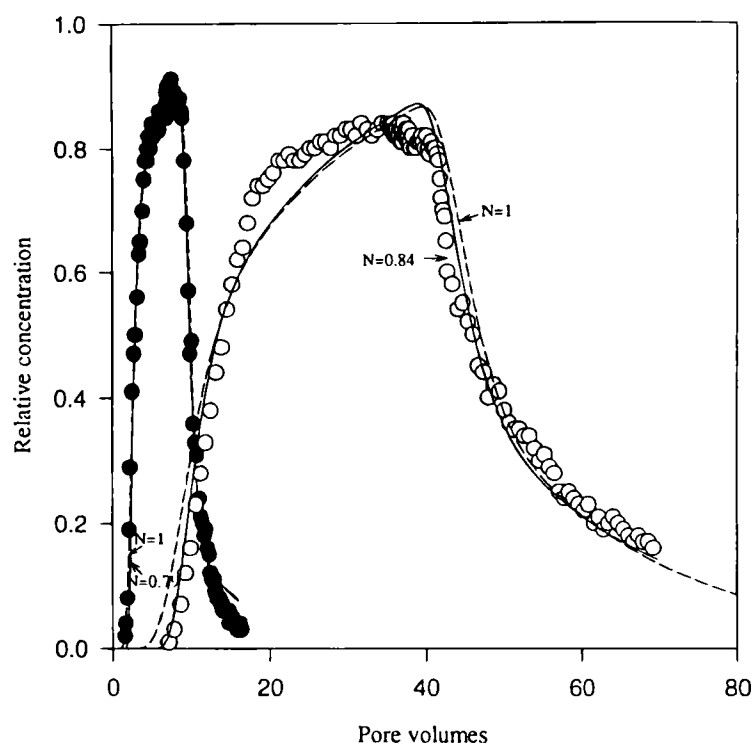


Fig. 5. Measured and simulated (line) BTC for 2,4-D in (●) Tokomaru and (○) Patua soil. Comparison of the simulated BTC for (---) linear and (—) nonlinear isotherms is shown.

cance of nonlinearity in comparison to non-equilibrium sorption in relation to movement of pesticides has been observed by others.^{6,9,35}

3.5 Significance of model parameters

The values of the four nondimensional parameters, P , R , β and ω obtained independently or by fitting the bicontinuum model to the experimental BTC of 2,4-D are presented in Table 4.

The Peclet number (P) represents the contribution of hydrodynamic dispersion to solute transport. The P value determined from the BTC of a non-sorbed solute ($^3\text{H}_2\text{O}$) was used to simulate the BTC of the sorbed solute (2,4-D). The estimated P value was 23.9 in the Tokomaru and 16.0 in the Patua soil. It has been shown that, for P values > 100 , the BTC approaches a

symmetrical and sigmoidal shape. The R values used in modelling column experiments were calculated using the K and N values determined from the batch sorption experiment. The calculated R values for 2,4-D were 4.52 and 20.81 in the Tokomaru and the Patua soils, respectively. The larger the R value, the greater the retardation of solute by soil and the lesser the mobility.

The other two unknowns (β and ω) are the most difficult to determine independently and a nonlinear least-square optimization program²⁴ was used to determine these two parameters. The term β represents the fraction of the sorption sites with instantaneous retardation (i.e. sorption), whereas ω represents the mass transfer coefficient. These two parameters specify the degree of non-equilibrium.

The β values for 2,4-D were 0.6 and 0.52, while the ω values were 0.30 and 0.66 in the Tokomaru and the

TABLE 4
Model Parameters for Simulation of the BTC of 2,4-D using the Bicontinuum Non-equilibrium Sorption Model

Soil	Parameter ^a						
	P	R	K	N	β	ω	k_2 (h^{-1})
Tokomaru	23.9	4.52	3.42	0.79	0.60	0.30	0.016
Patua	16.0	20.81	17.42	0.84	0.52	0.66	0.008

^a P = Peclet number. R = Retardation factor. K , N = Freundlich coefficients. β = Fraction of instantaneous retardation. ω = Ratio of hydrodynamic residence time to characteristic time for sorption (Damkohler number). k_2 = Rate constant.

Patua soils, respectively. The β values indicate that instantaneous sorption occurs in 60% and 52% of the sorption sites for the Tokomaru and the Patua soils, respectively. The β values obtained in this experiment are in general smaller than those obtained for other pesticides¹⁰ and for inorganic solutes.⁴ The value of β depends not only on the solute and sorbent characteristics, but also on the flow conditions.^{36,37} When the ω value is greater than 1, sorption is near equilibrium, whereas non-equilibrium prevails when ω values are smaller than 1.³⁸ The ω values obtained in this experiment were <1 which demonstrates the importance of non-equilibrium sorption processes for 2,4-D movement in the Tokomaru and the Patua soils. Similarly, ω values <1 have been reported for many organic pesticides, such as atrazine, simazine and alachlor,¹⁰ chlorsulfuron³⁹ and inorganic solutes, such as cadmium.⁴

The β and ω values obtained from the optimization program were used to calculate the kinetic rate constant (k_2) values (eqn 12(g)). The calculated k_2 values were 0.016 and 0.008 h⁻¹ for the Tokomaru and the Patua soils, respectively. The k_2 value for 2,4-D (a polar compound) observed in this experiment was considerably smaller than that for nonpolar organic chemicals reported in the literature.⁴⁰ The kinetic rate constant (k_2) for 2,4-D was twice as large for the Tokomaru soil with low organic carbon (3.15%) as for the Patua soil with high organic carbon (8.7%). A similar increase in k_2 value with a decrease in organic carbon content has been observed by other researchers^{1,40} and is indicative of a diffusive process into sorbent organic matter. It has been shown that diffusion within the matrix of sorbent organic matter or intra-organic matter diffusion is responsible for the observed non-equilibrium sorption during the movement of pesticides in soils.^{10,40}

4 CONCLUSIONS

Sorption of pesticides was greater in an allophanic soil with high organic matter content than in a non-allophanic soil with lower organic matter content. Sorption kinetic data for pesticides showed an initial rapid rate followed by a slower rate of sorption. Two non-ionic pesticides were less mobile than two ionic pesticides. There was an inverse relationship between K_d of the pesticide and the percentage leaching, indicating the importance of sorption to leaching of pesticides. In repacked soil columns, symmetrical BTCs were obtained for a non-sorbed solute (³H₂O), but asymmetrical BTCs were obtained for the sorbed solute (2,4-D). The CDE model with an equilibrium sorption process failed to simulate the BTCs for the sorbed solute (2,4-D) in repacked columns, whereas the CDE model with a bicontinuum non-equilibrium sorption process simulated the BTCs for 2,4-D. Intra-organic matter diffusion is a

likely reason for the non-equilibrium sorption observed during the movement of pesticides in soils.

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